1,2-Eliminations from $(\text{CH}_3)_2\text{NH}^+\text{CH}_2\text{CH}_3$ and $(\text{CH}_3)_2\text{NH}_2^+$: Guided Dissociations

Charles E. Hudson and David J. McAdoo

Department of Neuroscience and Cell Biology, University of Texas Medical Branch, Galveston, Texas, USA

1,2-Eliminations are a varied and extensive set of dissociations of ions in the gas phase. To understand better such dissociations, elimination of $\text{CH}_2=\text{CH}_2$ and CH_3CH_3 from $(\text{CH}_3)_2\text{NH}^+\text{CH}_2\text{CH}_3$ (**1**) and of CH_4 from $(\text{CH}_3)_2\text{NH}_2^+$ are characterized by quantum chemical calculations. Stretching of the CN bond to ethyl is followed by shift of an H from methyl to the bridging position in ethyl and then to N to reach $(\text{CH}_3)_2\text{NH}_2^+ + \text{CH}_2=\text{CH}_2$ from **1**. CH_3CH_3 elimination by H-transfer to C_2H_5^+ to form $\text{CH}_3\text{NH}^+=\text{CH}_2 + \text{CH}_3\text{CH}_3$ also takes place. $(\text{CH}_3)_2\text{NH}_2^+$ eliminates methane by CN bond extension followed by β -H-transfer to give $\text{CH}_2=\text{NH}^+ + \text{CH}_4$. Low-energy reactions resembling complex-mediated 1,2-eliminations occur and constitute a hitherto largely unrecognized type of reaction. As in many complex-mediated reactions, these reactions transfer H between incipient fragments. They are distinguished from complex-mediated processes by the fragments not being able to rotate freely relative to each other near the transition state for reaction, as they do in complexes. Most 1,2-eliminations are ion-neutral complex-mediated, occur by the just described lower energy reactions, have 1,1-like transition states, or utilize highly asynchronous 1,2 transition states. All of these avoid synchronized 1,2-transition states that would violate conservation of orbital symmetry. (J Am Soc Mass Spectrom 2008, 19, 1491–1499) © 2008 American Society for Mass Spectrometry

Elimination reactions have long been of interest with regard to whether and how elementary steps of organic species are synchronized. Dewar concluded that synchronous breaking of bonds is generally prevented by high-energy requirements for simultaneously breaking multiple bonds [1]. Williams and Hvistendahl concluded that some 1,2-eliminations of H_2 occur by high-energy, symmetry-forbidden 1,2-trajectories and others by allowed 1,1-transition states [2, 3]. Uggerud and coworkers further characterized 1,1-like transition states for 1,2-eliminations [4–6]. Uggerud concluded that orbital symmetry [7] cannot be used to predict the reaction trajectories for the 1,2-eliminations that do occur [4]. However, we conclude that formal 1,2-eliminations generally avoid violating conservation of orbital symmetry. They do this by occurring in separate steps (ion-neutral complex-mediated or parallel lower energy processes), utilizing non-forbidden 1,1-like transition states, or passing through sufficiently asynchronous 1,2-transition states that they are not symmetry forbidden [8]. To categorize 1,2-eliminations, we here use theory to characterize dissociations of $(\text{CH}_3)_2\text{NH}^+\text{CH}_2\text{CH}_3$ (**1**) to $(\text{CH}_3)_2\text{NH}_2^+ + \text{CH}_2=\text{CH}_2$, to $\text{CH}_3\text{NH}^+=\text{CH}_2 + \text{CH}_3\text{CH}_3$, to $\text{CH}_3\text{NH}^+=\text{CH}_2 + 2 \text{CH}_3$, and of $(\text{CH}_3)_2\text{NH}_2^+$ to $\text{CH}=\text{NH}_2^+ + \text{CH}_4$.

The most common 1,2-elimination by cations in the gas phase is probably bond cleavage to form an ion-

neutral complex followed by H-transfer between incipient partners, often accompanied by isomerization [9–16]. Complexes are considered to be intermediaries when a bond is extended to the point that the partners can rotate relative to each other [10, 11, 17, 18], and/or reactions occur between incipient fragments [10, 12, 15]. Such reactions are initiated by simple bond cleavages to associated fragments and completed by reactions between the partners.

Another common type of 1,2-elimination involves transition states that closely resemble those for 1,1-eliminations [2–6]. In contrast to synchronous 1,2-transition states, 1,1-transition states do not violate conservation of orbital symmetry [3–5]. This is probably why many non-complex-mediated reactions utilize 1,1-like transition states [5, 8, 19, 20].

In CH_4 elimination from $\text{CH}_3\text{CH}=\text{OH}^+$, formally a 1,2-elimination [20] that releases a large amount of translational energy [21], H moves from O to H and then to the CC bond to eliminate methane through a 1,1-transition state (Scheme 1). The HH distance at the transition state in Scheme 1 is 0.889 Å, i.e., this transition state contains a pentavalent carbon. H_2 ejections from C_2H_5^+ [22] and C_3H_7^+ [8] also transit hypervalent configurations.

Formation of a $[\text{CH}_3\text{CH}=\text{OH}]^+$ complex by cleavage of the CC bond in $\text{CH}_3\text{CH}=\text{OH}^+$ would begin at ca. 200 kJ mol⁻¹ above the threshold for methane elimination [19, 20]. Thus, this methane elimination occurs well below the energy at which fragments can

Address reprint requests to Dr. D. J. McAdoo, Department of Neuroscience and Cell Biology, University of Texas Medical Branch, 301 University Blvd., Galveston, TX 77555-1043, USA. E-mail: djmcaadoo@utmb.edu

form and independently rotate, so the reaction is not complex-mediated [17, 18]. The trajectory of this dissociation is guided by specific interactions between incipient fragments, in contrast to the much less restricted movement of partners in complexes. Such “guided reactions” are one focus of this work.

Alkenes are eliminated from secondary alkylphenyl ether ions via 1,2-syn transition states in parallel with complex-mediated 1,2-processes [23–27]. Parallel operation of two mechanisms was demonstrated by quantum chemical calculations and the stereospecificity/isotopic exchange inferred by modeling experimental results. In the latter, the abstraction of a β hydrogen/deuterium in the elimination of $C_4(H,D)_8$ from labeled 2-phenoxybutane ions was demonstrated by specific transfer of a β -H(D), and free rotation of partners was demonstrated by H-transfer from all positions of the side chain [26]. Morton and coworkers [27] established that dissociation of the 2-phenoxypropane ion, like the dissociation of $CH_3CH=OH^+$, has an onset below the threshold for complex-mediated dissociation [26]. Although this reaction has a 1,2-transition state, at the transition state the O-propyl C–O bond is essentially fully broken (2.688 Å long); the O has moved toward H_t ($ROH_t = 1.748$ Å) and H_t has moved only slightly away from its carbon ($RCH_t = 1.163$ Å [26]. Computations indicate that breaking the OC bonds in the eliminations of 2-butene from neutral and from protonated *m*-dimethylaminophenyl butyl ethers also precedes H-transfer from a β carbon to O [27]. All three of the reactions just described begin with substantial CO bond stretching and are followed by transfer of a β -hydrogen to O. The asynchronous nature of these reactions allows them to occur via 1,2 transition states.

$CH_2=CH_2$ elimination gives the base peak (m/z 46) in the CID spectrum of $(CH_3)_2NH^+CH_2CH_3$ (**1**), the system we will study. Comparison to the dissociation of $CH_3CH_2NH^+=CH_2$ [28] suggested that **1** eliminates $CH_2=CH_2$ according to Scheme 2. We studied $CH_2=CH_2$ eliminations from $(CH_3)_2NH^+CH_2CH_3$ because of the possibility of their being guided reactions [28].

Scheme 3 was suggested by Harrison and coworkers [29] to rationalize collision-induced alkane eliminations from protonated secondary and tertiary amines. We sought ethane elimination from **1** according to Scheme 3 because this reaction is symmetry forbidden if synchronous and because confirmation of the hypothesized mechanism would be the first demonstration of an alkane elimination by forming a CC bond.

Scheme 1

Scheme 2

Theory

Energies and geometries of stationary points and intrinsic reaction coordinates were obtained using the Gaussian 03 suite of programs [30]. Geometries were determined by MP2/6-311G (d,p) and QCISD/6-311G(d,p) quantum chemical methods. Energies were obtained at the same levels of theory and with the same basis sets as the geometries, except QCISD(T)/6-311G(d,p) energies were obtained at QCISD/6-311G(d,p) geometries. We considered configurations with all positive vibrational frequencies to be stable species, and configurations possessing one imaginary vibrational frequency were considered to be transition states. MP2/6-311G(d,p) theory was used to trace reaction pathways by intrinsic reaction coordinate (IRC) methods [31, 32]. Attractions between atoms of interest were assessed by determining Wiberg bond index matrix elements in the natural atomic orbital basis [33, 34], hereafter referred to as Wiberg bond indexes. Zero point energies and vibrational frequencies were computed at the MP2/6-311G(d,p) level and are unscaled.

B3LYP/6-31G(d) and B3LYP/6-311G(d,p) methods did not deal satisfactorily with the reaction

A transition state that led from **1** to a complex with an unbridged ethyl rather than to the products in Scheme 2 was found by B3LYP theory. However, this transition state and its associated force constants could not be optimized to a QCISD transition state. The main reason for this seemed to be inadequate treatment of the bridged ethyl cation by B3LYP theory. Because of this problem, we do not report B3LYP results.

Scheme 3

Table 1. Energetics of stationary points in the reaction $(\text{CH}_3)_2\text{NHCH}_2\text{CH}_3^+ \rightarrow \text{CH}_2=\text{CH}_2 + \text{CH}_4 + \text{CH}_2=\text{NH}_2^+$

Species	Energy (Hartrees)			
	MP2/6-311G(d,p)	QCISD/6-311G(d,p)	QCISD(T)//6-311G(d,p) ^a	ZPE (kJ mol ⁻¹)
^b $(\text{CH}_3)_2\text{NHCH}_2\text{CH}_3^+$ (1)	-213.541879	-213.610676	-213.637831	437.5
^b $\text{TS}(\mathbf{1} \rightarrow [(\text{CH}_3)_2\text{NH}_2^+ \text{C}_2\text{H}_4])$	-213.420918	-213.491958	-213.519426	412.9
^b $[(\text{CH}_3)_2\text{NH}_2^+ \text{C}_2\text{H}_4]$	-213.505830	-213.576687	-213.604194	425.5
C_2H_4	-78.344292	-78.372910	-78.384234	134.6
$(\text{CH}_3)_2\text{NH}_2^+$	-135.145502	-135.190028	-135.205351	287.9
^b $(\text{CH}_3)_2\text{NH}_2^+ + \text{C}_2\text{H}_4$	-213.489794	-213.562938	-213.589585	422.4
C_2H_5^+	-78.613435	-78.645128	-78.654922	162.3
$(\text{CH}_3)_2\text{NH}$	-134.772576	-134.813954	-134.830018	246.6
$\text{C}_2\text{H}_5^+ + (\text{CH}_3)_2\text{NH}$	-213.386011	-213.459082	-213.484940	408.9
$\text{C}_2\text{H}_5^\cdot$	-78.902961	-78.938260	-78.946769	158.8
$(\text{CH}_3)_2\text{NH}^\cdot$	-134.471400	-134.520771	-134.534912	241.1
$\text{C}_2\text{H}_5^\cdot + (\text{CH}_3)_2\text{NH}^\cdot$	-213.374361	-213.459031	-213.481681	399.9
$\text{TS}(\mathbf{1} \rightarrow \text{CH}_3\text{NH}^+=\text{CH}_2 + \text{C}_2\text{H}_6)$	-213.409532	-213.481390	-213.509889	411.8
^b $\text{TS}(\text{CH}_3\text{NH}_2\text{CH}_3^+ \rightarrow \text{CH}_2=\text{NH}_2^+ + \text{CH}_4)$	-134.984225	-135.034283	-135.049200	265.6
$\text{CH}_2=\text{NH}_2^+$	-94.721651	-94.747188	-94.757979	143.7
CH_4	-40.379234	-40.401643	-40.405945	119.4
^b $\text{C}_2\text{H}_4 + \text{CH}_2=\text{NH}_2^+ + \text{CH}_4$	-213.445177	-213.521741	-213.548158	397.7
$\text{CH}_3^\cdot$	-39.707238	-39.729163	-39.732299	79.1
$\text{CH}_3\text{NH}_2^\cdot$	-95.262556	-95.297936	-95.306495	165.2
^b $\text{CH}_3^\cdot + \text{CH}_3\text{NH}_2^\cdot + \text{C}_2\text{H}_4$	-213.314086	-213.400009	-213.423028	378.9
CH_3^+	-39.356189	-39.378985	-39.381151	84.1
CH_3NH_2	-95.587461	-95.615993	-95.626334	171.2
^b $\text{CH}_3^+ + \text{CH}_3\text{NH}_2 + \text{C}_2\text{H}_4$	-213.287942	-213.367888	-213.391719	389.9

^a Obtained for structures optimized at the QCISD/6-311G** level of theory.^b Values are for the combination of all products generated starting from **1**.

Results and Discussion

$\text{CH}_2 = \text{CH}_2$ elimination from $(\text{CH}_3)_2\text{NH}^+\text{CH}_2\text{CH}_3$ (1)

We hypothesized by analogy to the dissociation of $\text{CH}_3\text{CH}_2\text{NH}^+=\text{CH}_2$ [28] that **1** dissociates to $\text{CH}_2=\text{CH}_2 + \text{CH}_2=\text{NH}_2^+ + \text{CH}_4$ by loss of $\text{CH}_2=\text{CH}_2$ and then methane (Scheme 2). The loss of $\text{CH}_2=\text{CH}_2$ to give the base peak in the CID spectrum of **1** [29], the structure of the transition state located by theory and the identification of the dissociation products establish that **1** eliminates $\text{CH}_2=\text{CH}_2$ as in Scheme 2. Energies for relevant transition states and stable structures are given in Tables 1 and 2 for reactions of **1**, and a potential energy diagram for ethene elimination from **1** and subsequent methane elimination from $(\text{CH}_3)_2\text{NH}_2^+$ is given in Figure 1. QCISD/6-311G(d,p) structures of **1**, the complex $[(\text{CH}_3)_2\text{NH}_2^+ \text{CH}_2=\text{CH}_2]$ (brackets designate ion-neutral complexes unless otherwise specified) and a transition state that connects this complex to **1** are

Table 2. Energetics of stationary points in the reaction $(\text{CH}_3)_2\text{NHCH}_2\text{CH}_3^+ \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4 + \text{CH}_2=\text{NH}_2^+$

Species	Relative energy (kJ mol ⁻¹)		
	MP2/6-311G(d,p)	QCISD/6-311G(d,p)	QCISD(T)/6-311G(d,p) ^a
^b $(\text{CH}_3)_2\text{NHCH}_2\text{CH}_3^+$ (1)	0	0	0
^b $\text{TS}(\mathbf{1} \rightarrow [(\text{CH}_3)_2\text{NH}_2^+ \text{C}_2\text{H}_4])$	293.0	287.1	286.3
^b $[(\text{CH}_3)_2\text{NH}_2^+ \text{C}_2\text{H}_4]$	82.6	77.2	76.3
^b $(\text{CH}_3)_2\text{NH}_2^+ + \text{C}_2\text{H}_4$	121.6	110.2	111.6
$\text{C}_2\text{H}_5^+ + (\text{CH}_3)_2\text{NH}$	380.6	369.4	372.8
$\text{C}_2\text{H}_5^\cdot + (\text{CH}_3)_2\text{NH}^\cdot$	402.2	360.5	399.9
$\text{TS}(\mathbf{1} \rightarrow \text{CH}_3\text{NH}^+=\text{CH}_2 + \text{C}_2\text{H}_6)$	322	314	310
^b $\text{TS}(\text{CH}_3\text{NH}_2\text{CH}_3^+ \rightarrow \text{CH}_2=\text{NH}_2^+ + \text{CH}_4)$	522.8	496.9	499.3
^b $\text{C}_2\text{H}_4 + \text{CH}_2=\text{NH}_2^+ + \text{CH}_4$	214.1	193.7	195.6
$\text{CH}_3^\cdot + \text{CH}_3\text{NH}_2^\cdot + \text{C}_2\text{H}_4$	417.8	384	393.8
$\text{CH}_3^+ + \text{CH}_3\text{NH}_2 + \text{C}_2\text{H}_4$	619.1	589.8	588.6

^a Obtained for structures optimized at the QCISD/6-311G** level of theory.^b Values are for the combination of all products generated starting from **1**.

Figure 1. Potential energy diagram for the pathway from $(\text{CH}_3)_2\text{NH}^+\text{CH}_2\text{CH}_3$ to $\text{CH}_2=\text{NH}_2^+ + \text{CH}_4 + \text{CH}_2=\text{CH}_2$. Energies were obtained at the QCISD(T)/6-311G(d,p) level of theory and geometries by QCISD/6-311G(d,p) theory. The high-energy of the first transition state relative to the $[(\text{CH}_3)_2\text{NH}_2^+ + \text{CH}_2=\text{CH}_2]$ complex and substantial reverse critical energy for the dissociation thereof indicate that the partners separate very quickly after the transition state is passed toward the complex.

pictured in Figure 2. A second trajectory connecting 1 and this complex is described in the next section.

For convenient reference in the remainder of this paper, atoms in 1 are designated numerically as follows:

The bond lengths and angle that change most substantially in the course of $\text{CH}_2=\text{CH}_2$ elimination from 1 are plotted as a function of step number along the intrinsic reaction coordinate in Figure 3. These plots demonstrate that 1,2-elimination of $\text{CH}_2=\text{CH}_2$ from 1 takes place in several consecutive stages: (1) stretching of the $\text{C}^1\text{-N}$ bond, (2) revolution of H^1 around C^2 in C_2H_5 to bridge $\text{CH}_2=\text{CH}_2$, (3) transfer of H^1 to N, and (4) dissociation (Scheme 2).

C_2H_5^+ and $(\text{CH}_3)_2\text{NH}$ are well apart in the transition state for $\text{CH}_2=\text{CH}_2$ elimination: $\text{RC}^1\text{N}=2.6395 \text{ \AA}$ and $\text{RC}^2\text{N}=3.2908 \text{ \AA}$ (R is the distance between two specified atoms), so the C^1N bond is substantially broken, whereas transfer of H^1 to N is just beginning at this point ($\text{RC}^2\text{H}^1=1.2225 \text{ \AA}$; $\text{RH}^1\text{N}=2.1404 \text{ \AA}$). This transition state is quite asymmetric, the C^1H^1 and C^2H^1 distances being $1.4427 \text{ \AA}$ and $1.2225 \text{ \AA}$, respectively, and, as just noted, the RC^1N and RC^2N distances are substantially unequal. This transition state is much higher in energy (210 kJ mol^{-1}) than the symmetric $[\text{CH}_2=\text{CH}_2 \text{ NH}(\text{CH}_3)_2]^+$ complex that this transition state connects to 1 (Tables 1 and 2).

The C^1N bond is largely broken at the transition state ($\text{R} = 2.6395 \text{ \AA}$, Wiberg bond index = 0.094). H^1 is

transferring from the bridging position of C_2H_5^+ to N as the system moves from the transition state for dissociation of 1 toward the $(\text{CH}_3)_2\text{NH}_2^+ + \text{CH}_2=\text{CH}_2$ configuration. The relative positions of the partners shift slightly as H^1 transfers from C_2H_5^+ to $(\text{CH}_3)_2\text{NH}$ (Figure 2). The short RH^1C^1 and RH^1C^2 interatomic distances in the transition state (see above) versus the H^1C^1 and H^1C^2 distances of $2.3436 \text{ \AA}$ and $2.3436 \text{ \AA}$ in the complex demonstrate that transfer of H^1 to N occurs after the transition state is passed. Loss of $\text{CH}_2=\text{CH}_2$ from 1 has a large reverse critical energy (175 kJ mol^{-1}) so, like $\text{CH}_2=\text{CH}_2$ elimination from $\text{CH}_3\text{CH}_2\text{NH}^+=\text{CH}_2$, that dissociation of 1 is extremely rapid.

The trajectory for $\text{CH}_2=\text{CH}_2$ elimination from 1 in Scheme 2 is very similar to that for $\text{CH}_2=\text{CH}_2$ elimination from $\text{CH}_3\text{CH}_2\text{NH}^+=\text{CH}_2$ [28]: both involve CN bond stretching followed by revolution of a beta H around the carbon to which it is attached (C^2) to bridge the $\text{C}=\text{C}$ bond (Figure 3), and finally transfer of H^1 to N and dissociation [28]. Methane elimination from the propane ion [35], methane elimination from the *n*-butane ion [36], the dissociation of $\text{CH}_3\text{CH}_2\text{O}^+=\text{CH}_2$ [37, 38] and other dissociations [39, 40] also involve formation of bridged alkyl ions in conjunction with C-X bond extension, i.e., such sequences are common.

According to our Wiberg bond indexes, significant attraction exists between $(\text{CH}_3)_2\text{NH}$ and CH_3CH_2^+ at the transition state connecting 1 and $[(\text{CH}_3)_2\text{NH}_2^+ + \text{CH}_2=\text{CH}_2]$: the Wiberg bond index for $\text{H}^1\text{N} = 0.0099$, for N to the ethyl carbons the indexes equal 0.068 and 0.061, C^1 to $\text{H}^1 = 0.28$ and C^2 to $\text{H}^1 = 0.51$. The index for the HN bond is 0.79. Indexes between atoms in opposite

Figure 2. QCISD/6-311G(d,p) geometries for $(\text{CH}_3)_2\text{NH}_2^+\text{CH}_2\text{CH}_3$ (1) (top), the transition state leading from 1 to a $[\text{CH}_2=\text{CH}_2 (\text{CH}_3)_2\text{NH}_2^+]$ configuration (middle), and the corresponding complex (bottom). The structure of 1 is without remarkable features. In the transition state, a hydrogen from the C^2 methyl is moving to a bridging position in C_2H_5^+ (from which it will proceed to the nitrogen.) In the complex, $\text{CH}_2=\text{CH}_2$ is held symmetrically to $(\text{CH}_3)_2\text{NH}^+$ by attractions between the N and the $\text{CH}_2=\text{CH}_2$ carbons. The complex is symmetrical, having essentially identical distances between corresponding atoms and a plane of symmetry perpendicularly bisecting $(\text{CH}_3)_2\text{NH}^+$ and $\text{CH}_2=\text{CH}_2$.

partners (NC^1 , NC^2 , H^{N}) at the transition state from 1 sum to about 18% of the index for a covalent bond. This sum is about three times the corresponding one for

$[(\text{CH}_3)_2\text{NH}_2^+ \text{CH}_2=\text{CH}_2]$ (6% to 7%, see below). These attractions would prevent free relative rotation of partners, i.e., complex formation at and near the transition state, in the absence of excess internal energy. However, separate rotation of the partners probably does occur when there is sufficient internal energy in the system to overcome the attractive forces between the incipient fragments, i.e., complex-mediated elimination should appear and increase in importance with increasing internal energy above the onset for formation of the complex [26].

Another $\text{CH}_2=\text{CH}_2$ Elimination from 1

We also found a segment of another pathway from 1 to $\text{CH}_2=\text{CH}_2$ elimination, movement of C_2H_5^+ from a bridged $[(\text{CH}_3)_2\text{NH} \text{C}_2\text{H}_5^+]$ complex around a $(\text{CH}_3)_2\text{NH}$ methyl (Figure 4) and through a $(\text{CH}_3)_2\text{NH}_2^+ \text{CH}_2=\text{CH}_2$ configuration to products. The starting complex contained no imaginary frequencies and had a plane of symmetry containing H^{t} , H^{N} and N. The later configuration was identical to that of the complex in Figure 2, indicating joining of the two pathways late in the reactions. MP2/6-311G(d,p) computations placed a transition state between

Figure 3. Upper panel: IRC traces for C^1N bond-breaking and $\text{RC}^2\text{H}^{\text{t}}$ stretching (movement of H_t to a bridging position in C_2H_5^+). Lower panel: changes in the $\text{H}^{\text{t}}\text{C}^2\text{C}^1$ bond angle with movement of H_t away from its carbon of origin. The reaction starts with C^1N stretching, which is followed by revolution of H_t to a bridging position (lower panel), and finally transfer to N. The trace ended at the $[(\text{CH}_3)_2\text{NH}_2^+ \text{CH}_2=\text{CH}_2]$ complex. The units of the abscissa are number of steps along the intrinsic reaction coordinate.

Figure 4. Upper panel: Early complex on a second pathway to $\text{CH}_2=\text{CH}_2$ elimination from **1**. At this point, $\text{H}^\ddagger$ symmetrically bridges C^1 and C^2 and is substantially closer to C_2H_4 than it is to $(\text{CH}_3)_2\text{NH}$. $\text{H}^\ddagger$ points toward N while NH points away from $\text{H}^\ddagger$. Lower panel: Transition state for $\text{CH}_2=\text{CH}_2$ elimination involving migration of C_2H_5^+ around $(\text{CH}_3)_2\text{NH}$ followed by $\text{H}^\ddagger$ -transfer between the partners and dissociation. This complex is identical in structure to the corresponding complex in Figure 2, and is also likely to have a very fleeting existence due to the high reverse critical energy. C_2H_5^+ passes around a $(\text{CH}_3)_2\text{NH}$ methyl with $\text{H}^\ddagger$ pointing toward the methyl over the course of this reaction.

the complex and the later configuration at 359 kJ mol^{-1} , somewhat higher than the initially located transition states for $\text{CH}_2=\text{CH}_2$ and CH_3CH_3 eliminations (See below).

The existence of two pathways from **1** to $\text{CH}_2=\text{CH}_2$ elimination adds to evidence that reactions between incipient partners can follow distinct trajectories, as we have reported elsewhere [41]. Although the reorientation criterion appears to be satisfied by the movement of the partners around each other in this reaction, the two $\text{CH}_2=\text{CH}_2$ elimination pathways probably would not be distinct if the partners reorient freely relative to each other in the course of those reactions. There is little reorientation of the partners in the preceding $\text{CH}_2=\text{CH}_2$ elimination, at least not at the very low internal energies at which the reaction is sub-complex mediated. (We will use that term to refer to reactions that occur below the energies at which complex-mediated reactions take place.) Thus apparently a complex-mediated and a distinct sub-complex reaction both connect **1** to $[\text{CH}_2=\text{CH}_2 (\text{CH}_3)_2\text{NH}_2^+]$. Morton and coworkers previously reported the parallel occurrence of two such reactions (see above) [26].

CH_3CH_3 Elimination and CC Bond Formation from **1**

We also characterized C_2H_6 elimination from **1**, initially to explore whether CC bond formation can form alkanes and be eliminated (Scheme 3). The peak representing this dissociation is 65% as abundant as the base peak ($\text{CH}_2=\text{CH}_2$ elimination) in the high-energy CID spectrum of **1** [29], so this reaction occurs. C_2H_6 might be formed from **1** by abstraction of an alkyl group by the radical in an ion-alkyl radical complex or by concerted CC bond-breaking and making to give a 1,2-elimination (Scheme 3). Trajectories for 1,2-alkane eliminations were sought in a number of attempts by squeezing the C^3 methyl together with the C^2 methyl or the ethyl by bond stretching or by constricting bond angles. However, all of these efforts led instead to high-energy, sometimes anti-bonding, interactions, with no indication of CC bond formation. Therefore, alkane elimination by CC bond formation does not seem to be feasible.

A transition state for ethane elimination was found by feeding the high-energy point in one of the preceding searches into a transition state-seeking routine with normal run-stopping criteria suspended (NOEIGENTEST). This transition state was only 24 kJ mol^{-1} [QCISD(T)/6-311G(d,p) result] higher in energy than the lower energy transition state leading to $[(\text{CH}_3)_2\text{NH}_2^+ \text{CH}_2=\text{CH}_2]$. IRC calculations revealed that this transition state did not unite two methyls; instead, the reaction involved breaking the $\text{C}^1\text{--N}$ bond, 1,2- $\text{H}^\ddagger$ -shift in the ethyl and H-transfer from a N-methyl to C^2 as the latter is vacated by the $\text{H}^\ddagger$ -shift (Figure 5). Thus there are at least three pathways for dissociation of **1** that begin with CN bond extension and C_2H_5^+ isomerization. These reactions are separated by passage through different C_2H_5^+ $(\text{CH}_3)_2\text{NH}$ configura-

Figure 5. A transition state for ethane elimination from **1**. At this point, the C^1N bond is largely broken. Its proximity to C^1 and distance from C^2 demonstrates that $\text{H}^\ddagger$ has passed the symmetric bridging point and is approaching C^1 . The proximity of $\text{H}^\ddagger$ to C^3 and its distance from C^2 demonstrates that H transfer between those atoms is beginning. Thus at this transition state for CH_3CH_3 elimination from **1**, the bridging H is largely shifted toward C^1 whereas H-transfer between the fragments has just begun. Thus, these two processes are highly asynchronous.

Figure 6. QCISD/6-311G(d,p) structure of $\text{CH}_3\text{NH}_2^+\text{CH}_3$ and of the transition state for methane elimination therefrom. The reaction is initiated by stretching a CN bond; this is followed by H-transfer from N to C. At the transition state, the CN bond is largely broken ($\text{RCN}=2.485$ Å), and the H-CH₃ bond is just beginning to form ($\text{RCH}=1.8323$ Å).

tions, and are not freely accessible from each other's trajectories, i.e., they are guided.

We do not know of a formation of an alkane by the attack of an alkyl radical on an alkyl group, by a similar attack by an alkyl cation, or by concerted elimination of RR' (R and R' represent alkyl groups). The apparent absence of C-C bond formation from **1** is consistent with a preference for alkyl radicals to abstract H or halide atoms rather than carbon-containing groups [42]. This is reinforced by our failure to find a transition state for propane elimination from **1**. The inability of alkyl radicals to abstract alkyl radicals contrasts with the many H-abstractions by alkyl radicals that occur in ion-neutral complexes [16, 35, 36, 43].

Although the initial stages of the CH_3CH_3 elimination are similar to those of $\text{CH}_2=\text{CH}_2$ elimination from **1**, the final stages of the two reactions involve H-transfers in opposite directions, one direction producing $\text{CH}_2=\text{CH}_2$ and the other CH_3CH_3 . At the transition state for $\text{CH}_2=\text{CH}_2$ elimination, $\text{H}^\ddagger$ points toward $\text{CH}_3\text{NH}_2^+\text{CH}_3$, but it points away from $\text{CH}_3\text{NH}_2^+\text{CH}_3$ in the transition state for CH_3CH_3 elimination. At the

transition state for the former reaction, C^1N bond cleavage and the 1,2-H-shift are nearly complete while the $\text{H}^\ddagger$ -shift from the C^3 methyl to ethyl is in its early stages (Figure 5). Thus this 1,2-elimination is allowed by the temporal separation of the C^1N bond-breaking and the H-transfer. This existence of three different reaction trajectories initiated by cleavage of **1** to C_2H_5^+ - $(\text{CH}_3)_2\text{NH}$ further demonstrates that reactions between partners can occur in parallel by multiple trajectories. These appear to reflect differences in the initial trajectories of the reactants together with the local forces of attraction between the reactants.

The complex $[(\text{CH}_3)_2\text{NH}_2^+ \text{CH}_2=\text{CH}_2]$

We found a $[(\text{CH}_3)_2\text{NH}_2^+ \text{CH}_2=\text{CH}_2]$ complex (Figure 2) in a shallow potential minimum beyond and 210 kJ mol⁻¹ lower in energy than the transition state connecting **1** to this complex (Figure 1). In contrast to the transition state between this complex and **1**, this configuration is highly symmetric, all of its $\text{CH}_2=\text{CH}_2$ hydrogens being essentially equidistant from the N (3.6520 to 3.6574 Å) and nearly so from H_t (2.7362 to 2.7744 Å). The $\text{CH}_2=\text{CH}_2$ carbons are also equidistant from N (both 3.3449 Å) and from H_t (both 2.3436 Å). The $\text{CH}_2=\text{CH}_2$ axis is parallel to a line between C^3 and C^4 . The complex has a plane of symmetry that contains the NH_2 and perpendicularly bisects both $\text{CH}_3\text{NH}_2^+\text{CH}_3$ and $\text{CH}_2=\text{CH}_2$, $\text{RNH}_t = 1.033$ Å for the hydrogen between the N and C_2H_4 , and 1.023 Å for the other NH distance. Thus H_t is fully transferred from C_2H_5^+ to N in this complex.

As already discussed, **1** probably dissociates too rapidly for H-exchange to compete with dissociation when accessed by passage over the high barrier from **1** (Figure 1), although H-transfer between developing fragments occurs. However, since the ground state complex is in a shallow potential well (Figure 1), it can

Figure 7. Plots of RC^4N and RC^3H^1 in the IRC for elimination of methane from $\text{CH}_3\text{NH}_2^+\text{CH}_3$. CN breaking substantially leads H-transfer, demonstrating that this 1,2-elimination is highly asynchronous. The units of the abscissa are number of steps along the intrinsic reaction coordinate.

exist at energies below its dissociation threshold. There is less attraction between the partners in the complex (Wiberg bonding indexes for: $\text{CH}^\dagger$ for both ethyl carbons = 0.020, NC for both ethyl carbons = 0.006) than in the transition state, as the Wiberg indexes are smaller in the former. The Wiberg indexes for CH bonds in the intact methyls average 0.894; the index is 0.76 for NH and 0.69 for NH_2 . The C^1C^2 index = 1.82, demonstrating the presence of most of a π -bond between C^1 and C^2 . Summing the indexes representing interactions between the partners in the complex, that is those for the H_tCs and NC, gives 0.052, 6.8% of the NH index and 5.8% of the index for the intact CH, i.e., total bond orders between the partners are about 6% to 7% of those for a normal covalent bond.

The second step in the formation of $\text{CH}_2=\text{NH}_2^+$ from **1**,

provides another example of a 1,2-transition state. The structures of $\text{CH}_3\text{NH}_2^+\text{CH}_3$ and the transition state for methane elimination therefrom are given in Figure 6. In this dissociation, the C^3N bond stretches substantially before H-transfers between the developing fragments (Figure 7), so this reaction is quite asynchronous. At the transition state, $\text{RC}^4\text{N} = 2.4855 \text{ \AA}$, and H^1 is $1.1282 \text{ \AA}$ from C^3 , its carbon of origin; $\text{RH}^1\text{C}^4 = 1.8324 \text{ \AA}$, and $\text{RNH}^1 = 2.1164 \text{ \AA}$. Thus the reaction occurs in asynchronous stages: C–N bond stretching $\rightarrow$ H-transfer $\rightarrow$ dissociation. Mulliken and natural orbital population analysis placed most of the positive charge on the dissociating methyl and the least of it on the transferring H. Thus, the initial cleavage is heterolytic, although the transferring H, resembles a radical.

Wiberg bond indexes revealed three appreciable interactions between CH_3NH_2^+ and CH_3 at the transition state for methane elimination from $\text{CH}_3\text{NH}_2^+\text{CH}_3$. These indexes were: C^4N 0.093, C^3C^4 0.14, and C^4H^1 0.092. Other indexes were NH^1 0.021, C^3N 0.93, C^3H^1 0.80, and the index for each C^4H bond was 0.90. According to these indexes, at the transition state the C^4N bond was substantially broken, but the C^3H^1 bond was little stretched and the C^4H^1 bond was little formed. The indexes for the strongest attractions between the incipient fragments (the three just listed involving interactions with C^4 and the NH^1 interaction) add up to 39% of the index for a CH bond. Therefore, together they are strong enough to inhibit rotation of those fragments relative to each other, at least at energies substantially below the threshold for dissociation to $\text{CH}_3^\cdot + \text{CH}_3\text{NH}_2^+$. Thus this is a sub-complex mediated rather than a complex-mediated process. The C^4H^1 and C^3C^4 interactions also give this transition state some 1,1-character, although mechanistically it is best placed in the stretch-initiated, asynchronous H-transfer and sub-complex groups. The analogous

$(\text{CH}_3)_3\text{O}^+$ also eliminates methane by a methyl–O bond stretch followed by H-transfer [44]. Although the latter reaction follows essentially the same steps as would a corresponding reaction through an ion-neutral complex, it appears to be another example of a reaction at an energy (90 kJ mol^{-1}) too far below the threshold for dissociation to $\text{CH}_3^+ + \text{CH}_3\text{OCH}_3$ for the developing partners to rotate freely, i.e., for the reaction to be sub-complex-mediated.

Conclusions

1,2-Eliminations from cations in the gas phase take place by at least four different types of reactions. Type 1 passes through ion-neutral complexes. The second type involves attractions and relative movements between incipient fragments, but occurs at energies below those at which those fragments can move freely relative to each other. In it, movements of incipient fragments are guided by attractions between atoms in those fragments. This group has hitherto been little recognized [26]. Some trajectories of the first two types branch from a common stalk with the complex-mediated branch increasing in relative importance with increasing internal energy [26]. Mixtures of complex and subcomplex-mediated reactions are probably common. The third type goes through 1,1-like transition states and sometimes hypervalent stages. Most 1,1-like processes differ from complex-mediated reactions in that H-shift leads in the former while bond-breaking initiates the latter. We attribute the prominence of the 1,1 reactions to the conservation of orbital symmetry by avoiding synchronized 1,2-eliminations. The fourth type is asynchronous 1,2-eliminations initiated by bond extension and followed by H-transfer, e.g., dissociations of **1** and $\text{CH}_3\text{NH}^+\text{CH}_3$.

Our conclusions agree with the contention of Dewar that multibond processes are usually asynchronous [1]. However, whereas we attribute this to the avoidance of orbital symmetry constraints, Dewar concluded that multiple bonds do not break simultaneously because that would require an amount of energy roughly equal to the sum of the energies required to break each bonds individually [1]. Given that we recently found that H_2 elimination from $\text{CH}_3\text{CH}=\text{NH}^+\text{CH}_3$, an orbital symmetry allowed 1,4-process with a high reverse critical energy, is highly synchronous [45], we believe that orbital symmetry restraints significantly influence the mechanisms of 1,2-eliminations by preventing synchronized trajectories from being taken. This is not necessarily incompatible with the ideas of Dewar.

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